

CHARACTERIZATION OF COAL CHAR REACTIVITY BY THE NUMBER OF
ACTIVE SITES DURING CO₂ GASIFICATION

Z-B, Zhu
Department of Chemical Engineering
East China Institute of Technology
May Road, CHINA

T.Furusawa, T.Adschiri and T.Nozaki
Department of Chemical Engineering
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, 113 JAPAN

ABSTRACT

The present authors modified the transient kinetics method for the evaluation of the number of working active sites. The method was effectively used for the unified interpretation of both the reactivity and its dynamic change with increased conversion of nine different chars which are different in nature and origin. This method was developed furthermore for the evaluation of elemental reaction rate constants.

INTRODUCTION

Gasifier performance significantly depends on the coal char reactivity which are largely different among different chars. Thus the rational design and analyses of coal gasifier require the prediction of coal char reactivity as well as the sound understanding of gas-solid contact. Previous workers have tried to interpret the difference of the gasification rate by introducing various parameters including surface area(1) and the amount of metals in ash. Present authors have developed the new method to count the mol numbers of carbon atoms during gasification for the evaluation of char reactivity by transient kinetics experiment(2,3). The objective of the present study is the further development of this method for the evaluation of the elemental reaction rate constants.

EXPERIMENTAL

The experiments were conducted in a horizontal quartz tube reactor(i.d. 6 mm). The amount of chars of 15-85 mg was loaded in the middle part of the reactor tube. The reactor was heated up to the gasification temperature at the heating rate of 5 K/min in the pure nitrogen stream(2 m/s). The temperature of the bed was measured by a chromel-alumel thermocouple placed within the bed. The temperature difference through the bed was within 1 K at 1173K.

The nitrogen stream was switched over to carbon dioxide stream(2 m/s). The concentration of carbon monoxide produced was analyzed by FID after methanation. The variation of carbon monoxide concentration was followed intermittently at intervals of several seconds. The gasification rate of chars at atmospheric pressure are evaluated from the concentration of carbon monoxide, as follows.

$$\frac{dX}{dt} = \frac{C F}{2 \cdot 0.025} \frac{0.012}{w_0} \quad [s^{-1}] \quad (1)$$

where conversion of char was evaluated from the integrated amount of carbon monoxide produced. Then the carbon dioxide stream was switched over to nitrogen stream and the transient decay of carbon monoxide concentration was followed intermittently. After the concentration of carbon monoxide became so low as to be ignored, carbon dioxide were introduced again. This procedure was repeated several times to cover the whole range of conversion.

RESULTS AND DISCUSSION

Outline of our previous results and unified interpretation of char reactivity by number of working active sites

The number of working active sites was defined as the integrated amounts of carbon monoxide evolved after shutting off the carbon dioxide stream, as follows.

$$n = \int_0^t \frac{C F}{0.025} \frac{0.012}{w_0} dt \quad (2)$$

Previous investigation proved that the effects of both the backmixing of gases in the system on the number of active sites are negligible under the present experimental condition(2).

Figure 1 demonstrated that sixty times differences among the gasification rates of chars were fairly well interpreted by the difference in the number of working active sites at the temperature of 1173 K(3). The gasification rates normalized by the number of working active sites, $dX/dt/n$, decrease slightly with increased conversion but remain mostly constant during gasification, as shown in Fig.2(3). Thus evaluated results were plotted against reciprocal temperature in Fig.3. The result indicated that the rate per unit number of working active sites is the function of temperature alone. The activation energy of the reaction is around 125kJ/mol. Similar results of the rate normalized by surface area, $dX/dt/S(X)$, were obtained in our previous study(2,3).

Thus the present results support our previous results that surface area is an available parameter for the interpretation of both the difference and the dynamic change in gasification rate with increased conversion. Evaluated number of working active sites may be closely related to the number of intermediate species, such as surface oxide complex.

Development of new method

The rate constant of carbon monoxide desorption, K_d , after terminating gasification were also evaluated. The typical results of the desorption of carbon monoxide was shown in Fig.4. The results indicated that the partial pressure of carbon dioxide affects the number of working active sites but does not the desorption rate constant, K_d . The number of working active sites increased but the increasing rate decreased with increased partial pressure of carbon dioxide, as shown in Fig.5. The number of working active sites will be saturated at higher

pressure. Saturation mechanism is discussed later.

Figure 6 shows the typical dynamic change of carbon monoxide concentration, $C(t)$, after introducing carbon dioxide at the temperature of 1123 K for Taiheiyō coal char. Steady state concentration, $C_{st}(t)$, in the early period were evaluated by extrapolation of $C(t)$ over the latter period. The dynamic change of $[C(t)-C_{st}(t)]$ are shown in Fig.7. The rate constants, K , were evaluated over the range of carbon dioxide partial pressure from 15kPa to 100kPa. The dependency of the evaluated rate constant, K , on carbon dioxide partial pressure shown in Fig.8 can be described as follows.

$$K = L + J P_{CO_2} \quad (3)$$

The intercepts, I , are found to be almost the same as the desorption rate constants, K_d .

The following mechanism proposed by Ergun(3) and accepted widely can be used to interpret the above results.



The first step is the dissociative adsorption of carbon dioxide which produce the surface oxide complex and the second step is the desorption of surface oxide complex to produce carbon monoxide.

The dynamic response of carbon monoxide after introducing carbon dioxide, $C(t)$, can be expressed as

$$C(t) = \frac{0.025}{F} \frac{I_1 P_{CO_2} N}{I_1 P_{CO_2} + I_3} \frac{W_0}{0.012} [2I_3 + (I_1 P_{CO_2} - I_3) \exp(-(I_1 P_{CO_2} + I_3)t)] \quad (6)$$

The steady state concentration of carbon monoxide, C_{st} is

$$C_{st} = \frac{0.025}{F} \frac{2I_1 P_{CO_2} I_3 N}{[I_1 P_{CO_2} + I_3]} \frac{W_0}{0.012} \quad (7)$$

The the difference of the concentration, $C(t)-C_{st}$, is

$$C(t)-C_{st} = \frac{0.025}{F} \frac{2I_1 P_{CO_2} I_3 N}{I_1 P_{CO_2} + I_3} \frac{W_0}{0.012} \frac{(I_1 P_{CO_2} - I_3) \exp(-(I_1 P_{CO_2} + I_3)t)}{(I_1 P_{CO_2} + I_3)} \quad (8)$$

The rate constant of variation of $[C(t)-C_{st}]$ is $(I_1 P_{CO_2} + I_3)$ which is consistent with the P_{CO_2} dependence of the rate constant shown in Fig.8. Thus the intercept in the figure is I_3 , according to the above mechanism.

The dynamic change of carbon monoxide after shutting off the carbon dioxide is explained by the reaction of the second step, namely the desorption of surface oxide complex.

$$C_d(t) = 0.025 n_0 (W_0 / 0.012) \exp(-I_3 t) / F \quad (9)$$

Thus, the consistence of K_d and L evaluated above can be also interpreted.

The number of working active site is related to the partial pressure of carbon dioxide and the total number of active site, N , as

$$1/n = 1/N + (1/N)I_3/I_1P_{CO_2} \quad (10)$$

The reciprocal number of working active site, $(1/n)$, is plotted against $1/P_{CO_2}$ in Fig.9. The pressure dependence of the number of working active site, n , can be explained by Eq.(10). The slope of this figure is almost the same as the ratio of I_3 and $I_1P_{CO_2}$ which were evaluated above. The intercept is $1/N$ and thus the total number of active sites can be also evaluated.

CONCLUSION

The present authors has developed the new method to evaluate the number of working active sites during gasification. The difference of the reactivity among nine chars which are different in nature and origin could be fairly well interpreted by the number of working active sites. Dynamic change of reactivity with increased conversion could also be explained by the change of the number of working active sites.

The pressure dependency of working active site was investigated. The transient kinetics method was developed furthermore for the evaluation of elemental reaction rate constants and total number of active sites.

NOMENCLATURE

C	concentration of carbon monoxide [-]
C_{st}	steady state concentration of carbon monoxide [-]
F	gas flow rate [$m^3 s^{-1}$]
I	rate constant [s^{-1}]
J	rate constant [$s^{-1} atm^{-1}$]
K	rate constant [s^{-1}]
K_d	rate constant [s^{-1}]
L	rate constant [s^{-1}]
N	total number of active site [$mol_{carbon} mol^{-1}_{initial carbon}$]
n	number of working active site [$mol_{carbon} mol^{-1}_{initial carbon}$]
P	partial pressure [atm]
S	surface area [$m^2 kg^{-1}_{carbon}$]
T	absolute temperature [K]
t	time [s]
W_0	initial weight of carbon [kg]
X	conversion [-]

REFERENCES

- 1) Adschiri, T. and Furusawa, T., Fuel, 65, 927(1986)
- 2) Zhu, Z-B, Adschiri, T., Furusawa, T., Proceedings of Int. Symp. Coal Science 1987, pp515-518
- 3) Zhu, Z-B, Adschiri, T. and Furusawa, T., Proceedings of the 2nd Japan-China Symposium on Coal and C_1 Chemistry, 51
- 4) Ergun, S., J. Phys. Chem. 60, 480(1956)

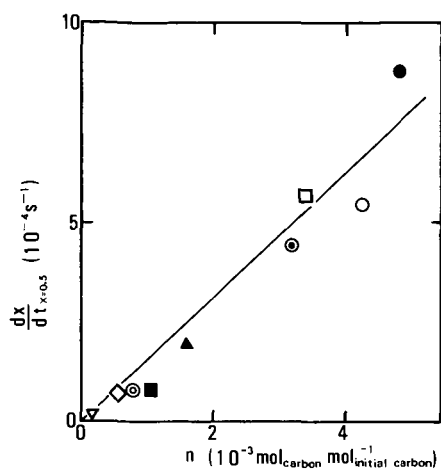


Figure 1. Relationship between the gasification rates and the number of working active sites.

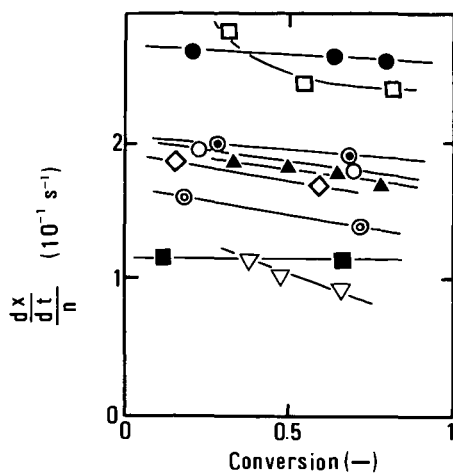


Figure 2. Gasification rates per unit number of working active sites.

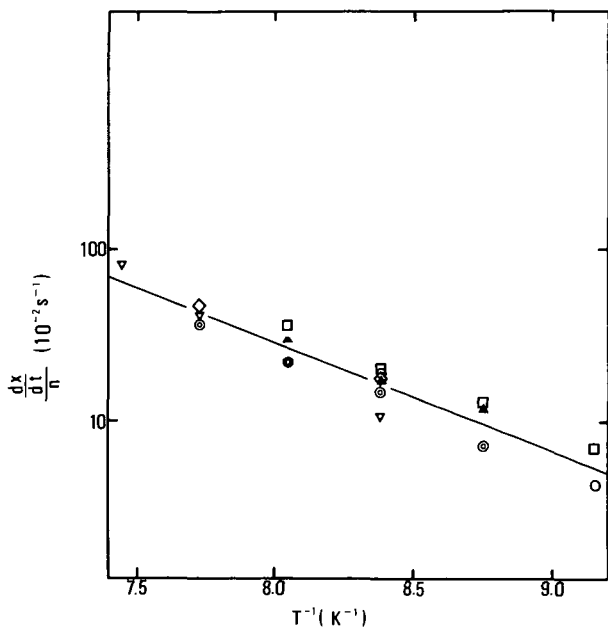


Figure 3. Arrhenius plot of gasification rates per unit number of working active sites.

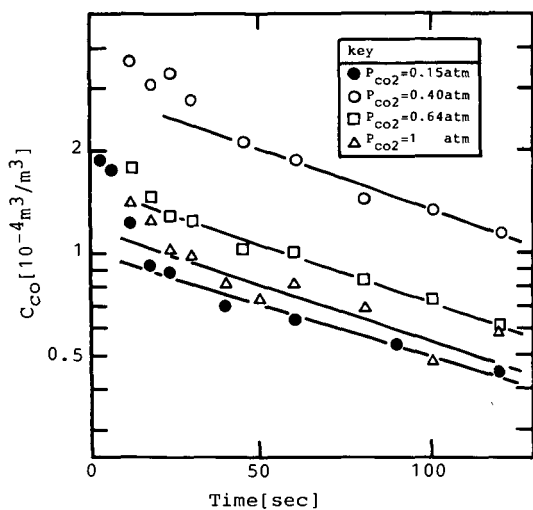


Figure 4. The typical desorption of carbon monoxide.

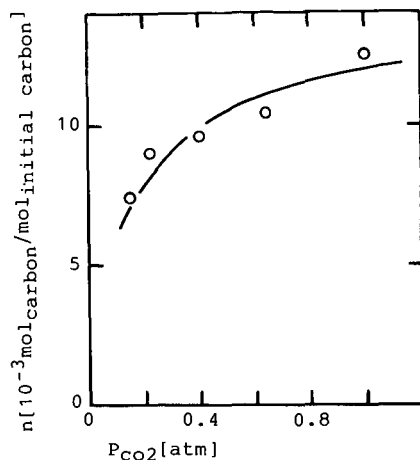


Figure 5. The number of working active sites Vs. partial pressure of carbon dioxide.

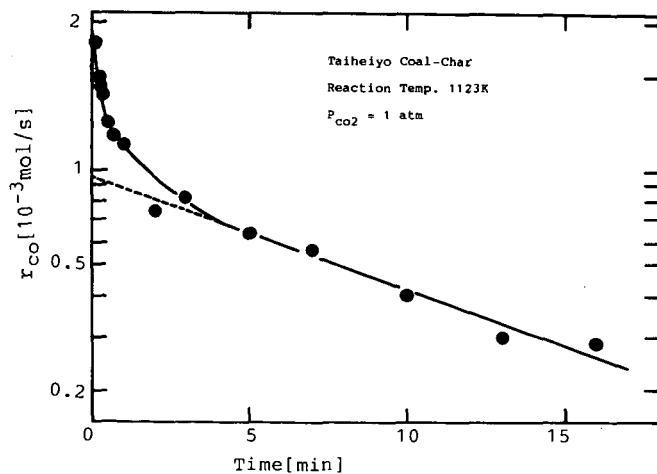


Figure 6. The typical dynamic change of carbon monoxide concentration.

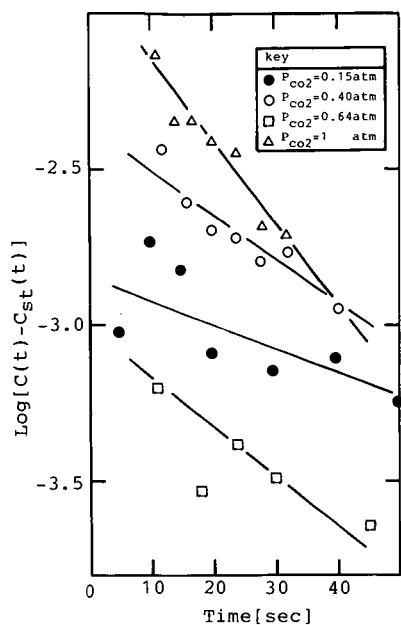


Figure 7. The dynamic change of $[C(t) - C_{st}(t)]$.

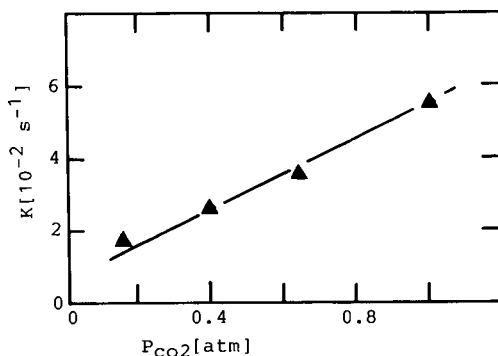


Figure 8. The rate constant K Vs. partial pressure of carbon dioxide.

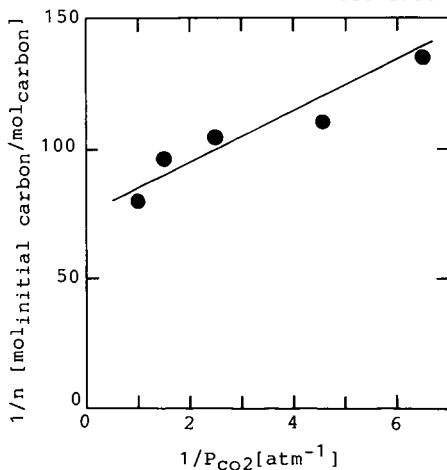


Figure 9. Relationship between the number of working active sites and the partial pressure of carbon dioxide.